

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>A61K 7/06, 7/50</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/35544</b> <b>(43) International Publication Date:</b> 2 October 1997 (02.10.97)
<b>(21) International Application Number:</b> PCT/US97/03695 <b>(22) International Filing Date:</b> 18 March 1997 (18.03.97) <b>(30) Priority Data:</b> 08/622,776                      27 March 1996 (27.03.96)                      US <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). <b>(72) Inventors:</b> GUSKEY, Susan, Marie; 10758 Moss Hill Lane, Montgomery, OH 45249 (US). ROYCE, Douglas, Allan; 10424 US 50, Aurora, IN 47001 (US). <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AU, BR, CA, CN, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CONDITIONING SHAMPOO COMPOSITIONS  <b>(57) Abstract</b>  Disclosed are aqueous conditioning shampoo compositions with improved stability and conditioning, which comprise an anionic detergent surfactant component and an organic, cross-linked, cationic hair conditioning polymer having a relatively high cationic charge density of from about 4 meq/gm to about 7 meq/gm. The cross-linked polymer consists essentially of a cross-linking agent and monomer units selected from the group consisting of dialkylaminoalkyl acrylamides, dialkylaminoalkyl methacrylamides, dialkylaminoalkyl acrylates, dialkylaminoalkyl methacrylates, and combinations thereof, wherein each of the monomer units in the cross-linked polymer are cationic at the pH of the shampoo composition.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## CONDITIONING SHAMPOO COMPOSITIONS

### FIELD OF THE INVENTION

The present invention relates to hair conditioning shampoo compositions which comprise crosslinked hair conditioning polymers which have a high cationic charge density.

### BACKGROUND OF THE INVENTION

Many shampoo products are commercially available or otherwise known, many of which also contain hair conditioning agents. These products provide users with both hair cleaning and conditioning performance from a single product, and conveniently allows for single application of a conditioner and shampoo during the shampooing process. Hair conditioning agents used in such products include silicone, hydrocarbon oils, fatty esters, cationic hair conditioning agents and combinations thereof.

Cationic hair conditioning agents (cationic surfactants, cationic polymers) are especially desirable for use in these hair conditioning shampoos to control static, detangle wet hair, and provide a silky, conditioned wet hair feel during and after rinsing. These cationic hair conditioning agents, however, often present compatibility problems when used in combination with many of the anionic surfactants known for use in shampoo compositions. Cationic surfactants as hair conditioning agents in the presence of some anionic deterative surfactants form a soluble ionic complex that does not deposit well on the hair. Such deposition is important for providing good conditioning performance. Other cationic surfactants as hair conditioning agents in the presence of anionic deterative surfactants form an insoluble complex which deposits well on hair but often does not provide good conditioning performance, and causes the hair to have a dirty, coated feel.

Cationic polymers have also been used as hair conditioning agents in shampoos, but these polymers tend to build up on the hair and cause the hair to have an unclean, coated feeling. Moreover, many of these cationic polymers have relatively high cationic charge density values which presents even more compatibility problems when used in combination with anionic surfactants. These highly charged cationic polymers typically form insoluble, highly viscous, clumps when combined with an anionic surfactant in a shampoo composition. The concentration and/or charge density of such cationic polymers, therefore, are often limited to help minimize the extent of these problems, or these highly charged polymers are used only in conditioning compositions that do not contain anionic surfactant. Limiting the concentration or amount of these polymers, however, can also limit the overall hair conditioning performance delivered from the conditioning shampoo composition.

It has now been found that select, highly charged, cationic hair conditioning polymers can be used in combination with an anionic deterative surfactant in a shampoo composition, which then provides improved hair conditioning performance and improved product stability. To realize such benefits, the

select polymers must be crosslinked, and have cationic charge density of from about 4.0 meq/gm to about 7 meq/gm, and consist essentially of a crosslinking agent in combination with a monomer unit selected from the group consisting dialkylaminoalkyl acrylamides, dialkylaminoalkyl methacrylamides, dialkylaminoalkyl acrylates, dialkylaminoalkyl methacrylates, and combinations thereof, wherein each of the monomer units is cationic at the pH of the composition.

It is therefore an object of the present invention to provide a conditioning shampoo composition with improved hair conditioning performance, and further to provide such a composition which contains a cationic hair conditioning polymer. It is a further object of the present invent to provide a conditioning shampoo composition with improved product stability which contains an anionic surfactant component in combination with a cationic hair conditioning polymer, and further to provide such a composition wherein the cationic polymers are crosslinked and have a relatively high cationic charge density of from about 4.0 meq/gm to about 7 meq/gm.

#### SUMMARY OF THE INVENTION

The present invention is directed to hair conditioning shampoo compositions which comprise (A) from about 5% to about 50% by weight of an anionic surfactant component selected from the group consisting of anionic surfactants, zwitterionic or amphoteric surfactants having an attached group that is anionic at the pH of the composition, and combinations thereof; (B) from about 0.025% to about 5% by weight of an organic, crosslinked, cationic polymer having a cationic charge density of from about 4 meq/gm to about 7 meq/gm, and wherein polymer consists essentially of a crosslinking agent in combination with a monomer unit selected from the group consisting dialkylaminoalkyl acrylamides, dialkylaminoalkyl methacrylamides, dialkylaminoalkyl acrylates, dialkylaminoalkyl methacrylates, and combinations thereof, wherein each of the monomer units is cationic at the pH of the composition; and (C) from about 20% to about 94% by weight of water. The crosslinked, highly charged, cationic polymers provide improved conditioning performance, and are physically compatible with the anionic deterative surfactant component of the composition.

#### DETAILED DESCRIPTION OF THE INVENTION

The shampoo compositions of the present invention can comprise, consist of, or consist essentially of the essential elements and limitations of the invention described herein, as well any of the additional or optional ingredients, components, or limitations described herein.

All percentages, parts and ratios are based upon the total weight of the shampoo compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in commercially available materials, unless otherwise specified.

As used herein, the term "soluble" refers to any material that is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% by weight of the material in water

at 25°C. Conversely, the term "insoluble" refers to all other materials that are therefore not sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% by weight of the other material in water at 25°C.

The shampoo compositions of the present invention, including the essential and some optional components thereof, are described in detail hereinafter.

#### Anionic Deterative Surfactant Component

The shampoo compositions of the present invention comprise an anionic deterative surfactant component to provide cleaning performance to the composition. The anionic deterative surfactant component in turn comprises anionic deterative surfactant, zwitterionic or amphoteric deterative surfactant which has an attached group that is anionic at the pH of the composition, or a combination thereof, preferably anionic deterative surfactant. Such surfactants should be physically and chemically compatible with the essential components described herein, or should not otherwise unduly impair product stability, aesthetics or performance.

Suitable anionic deterative surfactant components for use in the shampoo composition herein include those which are known for use in hair care or other personal care cleansing compositions. The concentration of the anionic surfactant component in the shampoo composition should be sufficient to provide the desired cleaning and lather performance, and generally range from about 5% to about 50%, preferably from about 8% to about 30%, more preferably from about 10% to about 25%, even more preferably from about 12% to about 18%, by weight of the composition.

Preferred anionic surfactants suitable for use in the shampoo compositions are the alkyl and alkyl ether sulfates. These materials have the respective formulae  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ , wherein R is alkyl or alkenyl of from about 8 to about 18 carbon atoms, x is an integer having a value of from 1 to 10, and M is a cation such as ammonium, alkanolamines, such as triethanolamine, monovalent metals, such as sodium and potassium, and polyvalent metal cations, such as magnesium, and calcium. The cation M should be selected such that the anionic deterative surfactant component is water soluble. Solubility of the surfactant will depend upon the particular anionic deterative surfactants and cations chosen.

Preferably, R has from about 8 to about 18 carbon atoms, more preferably from about 10 to about 16 carbon atoms, even more preferably from about 12 to about 14 carbon atoms, in both the alkyl and alkyl ether sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be synthetic or they can be derived from fats, e.g., coconut oil, palm kernel oil, tallow. Lauryl alcohol and straight chain alcohols derived from coconut oil or palm kernel oil are preferred. Such alcohols are reacted with between about 0 and about 10, preferably from about 2 to about 5, more preferably about 3, molar proportions of ethylene oxide, and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific non limiting examples of alkyl ether sulfates which may be used in the shampoo compositions of the present invention include sodium and ammonium salts of coconut alkyl triethylene glycol ether sulfate, tallow alkyl triethylene glycol ether sulfate, and tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, wherein the compounds in the mixture have an average alkyl chain length of from about 10 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide.

Other suitable anionic deterative surfactants are the water-soluble salts of organic, sulfuric acid reaction products conforming to the formula  $[R^1-SO_3-M]$  where  $R^1$  is a straight or branched chain, saturated, aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 18, carbon atoms; and M is a cation described hereinbefore. Non limiting examples of such deterative surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having from about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g.,  $SO_3$ ,  $H_2SO_4$ , obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated  $C_{10}$  to  $C_{18}$  n-paraffins.

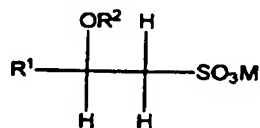
Still other suitable anionic deterative surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil or palm kernel oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil or palm kernel oil. Other similar anionic surfactants are described in U.S. Patent 2,486,921; U.S. Patent 2,486,922; and U.S. Patent 2,396,278, which descriptions are incorporated herein by reference.

Other anionic deterative surfactants suitable for use in the shampoo compositions are the succinates, examples of which include disodium N-octadecylsulfosuccinate; disodium lauryl sulfosuccinate; diammonium lauryl sulfosuccinate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; and dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic deterative surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. In this context, the term "olefin sulfonates" refers to compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid  $SO_2$ , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous  $SO_2$ , etc., when used in the gaseous form. The alpha-olefins from which the olefin sulfonates are derived are mono-olefins having from about 10 to about 24 carbon atoms, preferably from about 12 to about 16 carbon atoms.

Preferably, they are straight chain olefins. In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process. A non limiting example of such an alpha-olefin sulfonate mixture is described in U.S. Patent 3,332,880, which description is incorporated herein by reference.

Another class of anionic deterative surfactants suitable for use in the shampoo compositions are the beta-alkyloxy alkane sulfonates. These surfactants conform to the formula



where R<sup>1</sup> is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R<sup>2</sup> is a lower alkyl group having from about 1 to about 3 carbon atoms, preferably 1 carbon atom, and M is a water-soluble cation as described hereinbefore.

Preferred anionic deterative surfactants for use in the shampoo compositions include ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate, triethanolamine lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, and combinations thereof.

Suitable amphoteric or zwitterionic deterative surfactants for use in the shampoo composition herein include those which are known for use in hair care or other personal care cleansing composition, and which contain a group that is anionic at the pH of the shampoo composition. Concentration of such amphoteric deterative surfactants preferably ranges from about 0.5 % to about 20%, preferably from about 1% to about 10%, by weight of the composition. Non limiting examples of suitable zwitterionic or amphoteric surfactants are described in U.S. Patents 5,104,646 (Bolich Jr. et al.), U.S. Patent 5,106,609 (Bolich Jr. et al.), which descriptions are incorporated herein by reference.

Amphoteric deterative surfactants suitable for use in the shampoo composition are well known in the art, and include those surfactants broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic

substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group such as carboxy, sulfonate, sulfate, phosphate, or phosphonate.

Zwitterionic deterative surfactants suitable for use in the shampoo composition are well known in the art, and include those surfactants broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate or phosphonate. Zwitterionics such as betaines are preferred.

The shampoo compositions of the present invention may further comprise additional surfactants for use in combination with the anionic deterative surfactant component described hereinbefore. Suitable optional surfactants include nonionic surfactants, cationic surfactants, and combinations thereof. Any such surfactant known in the art for use in hair or personal care products may be used, provided that the optional additional surfactant is also chemically and physically compatible with the essential components of the shampoo composition, or does not otherwise unduly impair product performance, aesthetics or stability. The concentration of the optional additional surfactants in the shampoo composition may vary with the cleansing or lather performance desired, the optional surfactant selected, the desired product concentration, the presence of other components in the composition, and other factors well known in the art.

Non limiting examples of other anionic, zwitterionic, amphoteric or optional additional surfactants suitable for use in the shampoo compositions are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., and U.S. Patent 3,929,678, U.S. Patent 2,658,072; U.S. Patent 2,438,091; U.S. Patent 2,528,378, which descriptions are incorporated herein by reference.

#### **Cationic Hair Conditioning Polymer**

The shampoo compositions of the present invention comprise cationic, crosslinked, hair conditioning polymers having a relatively high, cationic charge density. These highly charged, cationic polymers, when crosslinked and used in combination with the anionic deterative surfactant component described hereinbefore, form a stable shampoo composition with improved conditioning performance. The concentration of the crosslinked polymer in the shampoo composition is from about 0.025% to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.25% to about 1%, by weight of the composition.

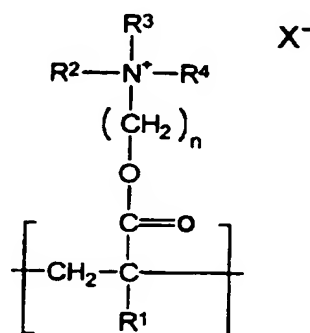
The hair conditioning polymers for use in the shampoo composition herein must be water dispersible, crosslinked, cationic polymers having a cationic charge density of from about 4 meq/gm to about 7 meq/gm, preferably from about 4 meq/gm to about 6 meq/gm, more preferably from about 4.2 meq/gm to about 5.5 meq/gm.

The hair conditioning polymers herein consist essentially of a crosslinking agent in combination with one or more cationic substituted monomer units, wherein the cationic substituent on each of the



monomer units is a quaternary ammonium or protonated amino group (acid addition salt), and wherein the monomer units are selected from the group consisting of cationic substituted dialkylaminoalkyl acrylamides, dialkylaminoalkyl methacrylamides, dialkylaminoalkyl acrylates, dialkylaminoalkyl methacrylates, and combinations thereof, preferably dialkylaminoalkyl acrylamides, dialkylaminoalkyl methacrylamides, and combinations thereof.

Preferred cationic substituted monomers are the cationic substituted dialkylaminoalkyl acrylates, dialkylaminoalkyl methacrylates, and combinations thereof. These preferred monomers conform to the formula



wherein  $\text{R}^1$  is hydrogen, methyl or ethyl; each of  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are independently hydrogen or a short chain alkyl having from about 1 to about 8 carbon atoms, preferably from about 1 to about 5 carbon atoms, more preferably from about 1 to about 2 carbon atoms;  $n$  is positive integer having a value of from about 1 to about 8, preferably from about 1 to about 4; and  $\text{X}$  is an anionic counterion. The nitrogen attached to  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  may be a protonated amine (primary, secondary or tertiary), but is preferably a quaternary ammonium wherein each of  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are alkyl groups.

The anionic counterion ( $\text{X}^-$ ) in association with the cationic conditioning polymers may be any known counterion so long as the polymers remain soluble or dispersible in water, in the shampoo composition, or in a coacervate phase of the shampoo composition, and so long as the counterions are physically and chemically compatible with the essential components of the shampoo composition or do not otherwise unduly impair product performance, stability or aesthetics. Non limiting examples of such counterions include halides (e.g., chlorine, fluorine, bromine, iodine), sulfate and methylsulfate.

The crosslinking agent herein may be any conventional or otherwise known crosslinking material for use with the cationic substituted monomer units described hereinbefore. These crosslinking agents are typically materials that contain two or more unsaturated functional groups, which are reacted with the monomer units of the polymer to form either links or covalent bonds between two or more individual polymer chains or between two or more sections of the same polymer chain. Non limiting examples of suitable crosslinking agents include methylenebisacrylamides, diacrylates, dimethacrylates, di-vinyl aryl (e.g. di-vinyl phenyl ring) compounds, polyalkenyl polyethers of polyhydric alcohols, allyl acrylates.

vinylalkylacrylates, and polyfunctional vinylidenes. Specific non limiting examples of such crosslinking agents include ethylene glycol, propylene glycol, butylene glycol, di-(meth)acrylate, di-(meth)acrylamide, cyanomethylacrylate, vinyloxyethylmethacrylate, allyl pentaerythritol, trimethylolpropane diallylether, allyl sucrose, butadiene, isoprene, 1,4 di-ethylene benzene, divinyl naphthalene, ethyl vinyl ether, methyl vinyl ether, and allyl acrylate. Other suitable crosslinking agents include formaldehyde and glyoxal. Preferred is the methylenebisacrylamide crosslinking agent.

Widely varying amounts of the crosslinking agent can be employed depending upon the properties desired in the final polymer, e.g. viscosifying effect. The crosslinking agent will typically comprise from about 1 ppm to about 10,000 ppm, preferably from about 5 ppm to about 750 ppm, more preferably from about 25 ppm to about 500 ppm, even more preferably from about 100 ppm to about 500 ppm, and most preferably from about 250 ppm to about 500 ppm of the total weight of the polymer on a weight/weight basis.

The intrinsic viscosity of the crosslinked, cationic polymer herein can be measured to more specifically characterize the polymer for purposes of the present invention. The intrinsic viscosity of the crosslinked polymer as measured in a one molar sodium chloride solution at 25°C is generally above 6, preferably from about 8 to 14. The average molecular weight of these crosslinked cationic polymers ranges generally from about 1 million to about 30 million. The specific molecular weight is not critical and lower or higher weight average molecular weights can be used. The crosslinked polymers are preferably characterized in a 1.0% solution of the polymer in deionized water to have a viscosity, at 25°C, of at least about 20,000 centipoise, more preferably at least about 30,000 centipoise, when measured at 20 RPM by a Brookfield RVT (Brookfield Engineering Laboratories, Inc. Stoughton, MA, USA).

These crosslinked cationic polymers can be prepared by methods well known in the art. For example, these polymers can be made by polymerization of an aqueous solution containing from about 20% to about 60%, generally from about 25% to about 40%, by weight monomer, in the presence of an initiator (usually redox or thermal) until the polymerization terminates. The crosslinking agent can also be added to the solution of the monomers to be polymerized, to incorporate it into the polymer. In the polymerization reactions, the temperature generally starts between about 0° and 95°C. The polymerization can be conducted by forming a reverse phase dispersion of an aqueous phase of the monomers (and also any additional crosslinking agents) into a nonaqueous liquid, e.g. mineral oil, lanolin, isododecane, oleyl alcohol, and other volatile and nonvolatile esters, ethers, and alcohols, and the like.

A non limiting example of a preferred crosslinked cationic polymer for use in the shampoo composition, and as described hereinabove, is Polyquaternium 37. This preferred crosslinked polymer can be used alone in the shampoo composition or in a suitable carrier such as mineral oil or propylene glycol dicaprylate/dicaprate. This polymer is commercially available as a mineral oil dispersion also containing PPG-1 trideceth-6 as a dispersing aid, from Allied Colloids Ltd, Norfolk, Virginia, U.S.A., under the trade

name Salcare® SC95 or as a dispersion in propylene glycol dicaprylate/dicaprate also containing PPG-1 trideceth-6 as a dispersing aid, from Allied Colloids Ltd, (Norfolk, VA) under the trademark Salcare® SC96.

#### Water

5 The shampoo compositions of the present invention are aqueous systems which comprise from about 20% to about 94%, preferably from about 50% to about 90%, more preferably from about 60% to about 85%, water by weight of the composition.

#### Optional Components

10 The shampoo compositions of the present invention may further comprise one or more optional components known for use in hair care or personal care products, provided that the optional components are physically and chemically compatible with the essential component described herein, or do not otherwise unduly impair product stability, aesthetics or performance. Concentrations of such optional components typically and individually range from about 0.001% to about 10% by weight of the shampoo compositions.

15 Non limiting examples of optional components for use in the shampoo composition include anti static agents, anti dandruff agents, conditioning agents (hydrocarbon oils, fatty esters) dyes, organic solvents or diluents, pearlescent aids, foam boosters, additional surfactants or cosurfactants (nonionic, cationic), pediculocides, pH adjusting agents, perfumes, preservatives, proteins, skin active agents, styling polymers, sunscreens, vitamins, and viscosity adjusting agents.

20 The shampoo composition of the present invention may further comprises a suspending or thickening agent. Suitable suspending agents for such materials are well known in the art, and include crystalline and polymeric suspending or thickening agents. Crystalline suspending agents are preferred, and include known acyl derivatives and amine oxides, and are described in U.S. Patent 4,741,855, which description is incorporated herein by reference.

25 Non limiting examples of optional polymeric thickening agents for use in the shampoo composition include carboxyvinyl polymers, cellulose ethers, guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, and xanthan gum. Suspending or thickening agents are described in U.S. Patent 2,798,053, U.S. Patent 4,686,254, U.S. Patent 4,788,006, and U.S. Patent 5,275,761, which descriptions are incorporated herein by reference. The optional  
30 suspending or thickening agents are described in more detail hereinafter.

The shampoo compositions of the present invention also preferably comprises a silicone hair conditioning agent, more preferably a silicone hair conditioning agent in combination with an optional  
35 suspending agent for the silicone. The silicone hair conditioning agent is preferably non volatile, and is preferably present in the shampoo composition at concentrations ranging from about 0.01% to about 10%, by weight of the shampoo composition. Non limiting examples of suitable silicone hair conditioning

agents, and optional suspending agents for the silicone, are described in U.S. Reissue Patent 34,584 (Grote et al.), U.S. Patents 5,104,646 (Bolich Jr. et al.), U.S. Patent 5,106,609 (Bolich Jr. et al.), which descriptions are incorporated herein by reference. The optional silicone hair conditioning agent, and optional suspending agents for the optional silicone, are described in more detail hereinafter.

#### Optional Silicone Hair Conditioning Agent

The shampoo compositions of the present invention may further comprise an optional silicone hair conditioning agent at concentrations effective to provide hair conditioning benefits. Such concentrations range from about 0.01% to about 10%, preferably from about 0.1% to about 8%, more preferably from about 0.1% to about 5%, most preferably from about 0.2% to about 3%, by weight of the shampoo compositions.

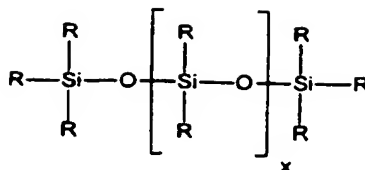
The optional silicone hair conditioning agents are insoluble in the shampoo compositions, and are preferably nonvolatile. Typically it will be intermixed in the shampoo composition so as to be in the form of a separate, discontinuous phase of dispersed, insoluble particles, also referred to as droplets. These droplets are typically suspended with an optional suspending agent described hereinafter. The optional silicone hair conditioning agent phase will comprise a silicone fluid hair conditioning agent such as a silicone fluid and can also comprise other ingredients, such as a silicone resin to improve silicone fluid deposition efficiency or enhance glossiness of the hair (especially when high refractive index (e.g. above about 1.46) silicone conditioning agents are used (e.g. highly phenylated silicones).

The optional silicone hair conditioning agent phase may comprise volatile silicone, nonvolatile silicone, or combinations thereof. Typically, if volatile silicones are present, it will be incidental to their use as a solvent or carrier for commercially available forms of nonvolatile silicone materials ingredients, such as silicone gums and resins.

The optional silicone hair conditioning agents for use in the shampoo compositions preferably have a viscosity of from about 20 to about 2,000,000 centistokes, more preferably from about 1,000 to about 1,800,000 centistokes, even more preferably from about 50,000 to about 1,500,000 centistokes, most preferably from about 100,000 to about 1,500,000 centistokes, as measured at 25°C.

Optional silicone fluids include silicone oils which are flowable silicone materials having a viscosity of less than 1,000,000 centistokes, preferably between about 5 and 1,000,000 centistokes, more preferably between about 10 and about 100,000 centistokes, at 25°C. Suitable silicone oils include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and combinations thereof. Other insoluble, nonvolatile silicone fluids having hair conditioning properties can also be used.

Optional silicone oils include polyalkyl or polyaryl siloxanes which conform to the following formula (I)



where R is aliphatic, preferably alkyl or alkenyl, or aryl, R can be substituted or unsubstituted, and x is an integer from 1 to about 8,000. Suitable unsubstituted R groups include alkoxy, aryloxy, alkaryl, arylalkyl, arylalkenyl, alkamino, and ether-substituted, hydroxyl-substituted, and halogen-substituted aliphatic and aryl groups. Suitable R groups also include cationic amines and quaternary ammonium groups.

The aliphatic or aryl groups substituted on the siloxane chain may have any structure so long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the shampoo compositions, are chemically stable under normal use and storage conditions, are insoluble in the shampoo compositions herein, and are capable of being deposited on and conditioning the hair.

The two R groups on the silicon atom of each monomeric silicone unit may represent the same or different groups. Preferably, the two R groups represent the same group.

Preferred alkyl and alkenyl substituents are C<sub>1</sub>-C<sub>5</sub> alkyls and alkenyls, more preferably from C<sub>1</sub>-C<sub>4</sub>, most preferably from C<sub>1</sub>-C<sub>2</sub>. The aliphatic portions of other alkyl-, alkenyl-, or alkynyl-containing groups (such as alkoxy, alkaryl, and alkamino) can be straight or branched chains and preferably have from one to five carbon atoms, more preferably from one to four carbon atoms, even more preferably from one to three carbon atoms, most preferably from one to two carbon atoms. As discussed above, the R substituents hereof can also contain amino functionalities, e.g. alkamino groups, which can be primary, secondary or tertiary amines or quaternary ammonium. These include mono-, di- and tri- alkylamino and alkoxyamino groups wherein the aliphatic portion chain length is preferably as described above. The R substituents can also be substituted with other groups, such as halogens (e.g. chloride, fluoride, and bromide), halogenated aliphatic or aryl groups, and hydroxy (e.g. hydroxy substituted aliphatic groups). Suitable halogenated R groups could include, for example, tri-halogenated (preferably fluoro) alkyl groups such as -R<sup>1</sup>-C(F)<sub>3</sub>, wherein R<sup>1</sup> is C<sub>1</sub>-C<sub>3</sub> alkyl. Examples of such polysiloxanes include polymethyl -3,3,3 trifluoropropylsiloxane.

Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane is especially preferred. Other suitable R groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The three R groups on the end caps of the silicone may also represent the same or different groups.

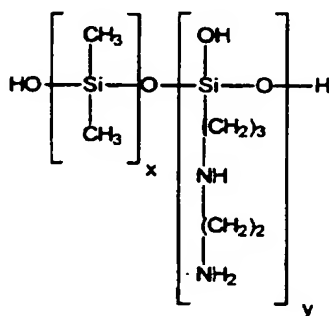
The nonvolatile polyalkylsiloxane fluids that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, from the General Electric Company in their Viscasil R and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

The polyether siloxane copolymers that may be used include, for example, a polypropylene oxide modified polydimethylsiloxane (e.g., Dow Corning DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used. The ethylene oxide and polypropylene oxide concentrations must be sufficiently low to prevent solubility in water and the composition hereof.

Suitable alkylamino substituted silicones include those which conform to the following structure

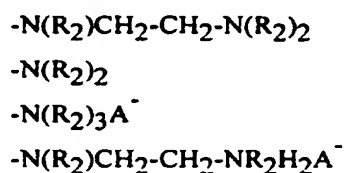
(II)



wherein x and y are integers. This polymer is also known as "amodimethicone".

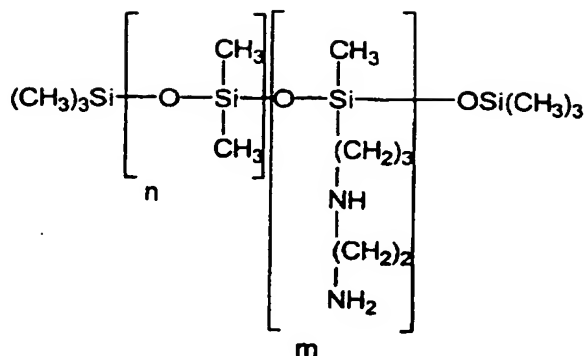
Suitable cationic silicone fluids include those which conform to the formula (III)

$(\text{R}_1)_a \text{G}_{3-a} - \text{Si} - (-\text{OSiG}_2)_n - (-\text{OSiG}_b(\text{R}_1)_{2-b})_m - \text{O} - \text{SiG}_{3-a}(\text{R}_1)_a$ , wherein G is selected from the group consisting of hydrogen, phenyl, hydroxy,  $\text{C}_1$ - $\text{C}_8$  alkyl and preferably methyl; a is 0 or an integer having a value from 1 to 3, preferably 0; b is 0 or 1, preferably 1; the sum  $n+m$  is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10;  $\text{R}_1$  is a monovalent radical conforming to the formula  $\text{C}_q\text{H}_{2q}\text{L}$  in which q is an integer having a value of from 2 to 8 and L is selected from the following groups:

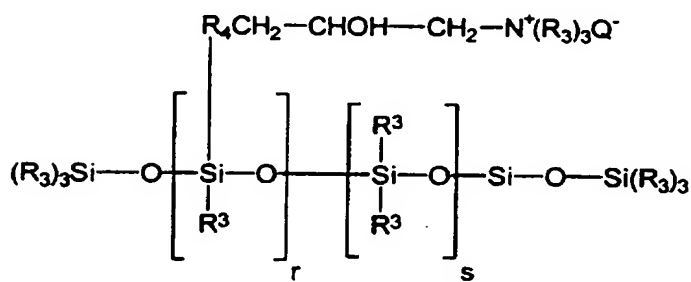


in which  $\text{R}_2$  is selected from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and  $\text{A}^-$  is a halide ion.

An especially preferred cationic silicone corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):



Other silicone cationic polymers which can be used in the shampoo compositions are represented by the formula (V):



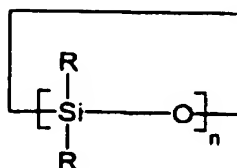
where  $\text{R}^3$  denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl;  $\text{R}_4$  denotes a hydrocarbon radical, preferably a  $\text{C}_1$ - $\text{C}_{18}$  alkylene radical or a  $\text{C}_1$ - $\text{C}_{18}$ , and more preferably  $\text{C}_1$ - $\text{C}_8$ , alkyleneoxy radical;  $\text{Q}^-$  is a halide ion, preferably chloride;  $r$  denotes an average statistical value from 2 to 20, preferably from 2 to 8;  $s$  denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCARE SILICONE ALE 56."

Other optional silicone fluids are the insoluble silicone gums. These gums are polyorganosiloxane materials having a viscosity at  $25^\circ\text{C}$  of greater than or equal to 1,000,000 centistokes. Silicone gums are described in U.S. Patent 4,152,416; Noll and Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968; and in General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76, all of which are incorporated herein by reference. The silicone gums will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000, specific examples of which include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof.

Another category of nonvolatile, insoluble silicone fluid conditioning agents are the high refractive index silicones, having a refractive index of at least about 1.46, preferably at least about 1.48, more preferably at least about 1.52, most preferably at least about 1.55. The refractive index of the

polysiloxane fluid will generally be less than about 1.70, typically less than about 1.60. In this context, polysiloxane "fluid" includes oils as well as gums.

The high refractive index polysiloxane fluid includes those represented by general Formula (I) above, as well as cyclic polysiloxanes such as those represented by Formula (VI) below:



wherein R is as defined above, n is from about 3 to about 7, preferably from 3 to 5.

The high refractive index polysiloxane fluids contain a sufficient amount of aryl-containing R substituents to increase the refractive index to the desired level, which is described above. In addition, R and n must be selected so that the material is nonvolatile, as defined above.

Aryl-containing substituents contain alicyclic and heterocyclic five and six membered aryl rings, and substituents containing fused five or six membered rings. The aryl rings themselves can be substituted or unsubstituted. Substituents include aliphatic substituents, and can also include alkoxy substituents, acyl substituents, ketones, halogens (e.g., Cl and Br), amines, etc. Exemplary aryl-containing groups include substituted and unsubstituted arenes, such as phenyl, and phenyl derivatives such as phenyls with  $C_1$ - $C_5$  alkyl or alkenyl substituents, e.g., allylphenyl, methyl phenyl and ethyl phenyl, vinyl phenyls such as styrenyl, and phenyl alkynes (e.g. phenyl  $C_2$ - $C_4$  alkynes). Heterocyclic aryl groups include substituents derived from furan, imidazole, pyrrole, pyridine, etc. Fused aryl ring substituents include, for example, naphthalene, coumarin, and purine.

In general, the high refractive index polysiloxane fluids will have a degree of aryl-containing substituents of at least about 15%, preferably at least about 20%, more preferably at least about 25%, even more preferably at least about 35%, most preferably at least about 50%. Typically, although it is not intended to necessarily limit the invention, the degree of aryl substitution will be less than about 90%, more generally less than about 85%, preferably from about 55% to about 80%.

The polysiloxane fluids are also characterized by relatively high surface tensions as a result of their aryl substitution. In general, the polysiloxane fluids hereof will have a surface tension of at least about 24 dynes/cm<sup>2</sup>, typically at least about 27 dynes/cm<sup>2</sup>. Surface tension, for purposes hereof, is measured by a de Nouy ring tensiometer according to Dow Corning Corporate Test Method CTM 0461, November 23, 1971. Changes in surface tension can be measured according to the above test method or according to ASTM Method D 1331.

Preferred high refractive index polysiloxane fluids have a combination of phenyl or phenyl derivative substituents (preferably phenyl), with alkyl substituents, preferably  $C_1$ - $C_4$  alkyl (most



preferably methyl), hydroxy, C<sub>1</sub>-C<sub>4</sub> alkylamino (especially -R<sup>1</sup>NHR<sup>2</sup>NH<sub>2</sub> where each R<sup>1</sup> and R<sup>2</sup> independently is a C<sub>1</sub>-C<sub>3</sub> alkyl, alkenyl, and/or alkoxy. High refractive index polysiloxanes are available from Dow Corning Corporation (Midland, Michigan, U.S.A.) Huls America (Piscataway, New Jersey, U.S.A.), and General Electric Silicones (Waterford, New York, U.S.A.).

5 It is preferred to utilize high refractive index silicones in solution with a spreading agent, such as a silicone resin or a surfactant, to reduce the surface tension by a sufficient amount to enhance spreading and thereby enhance glossiness (subsequent to drying) of hair treated with the composition. In general, a sufficient amount of the spreading agent to reduce the surface tension of the high refractive index polysiloxane fluid by at least about 5%, preferably at least about 10%, more preferably at least about 15%,  
10 even more preferably at least about 20%, most preferably at least about 25%. Reductions in surface tension of the polysiloxane fluid/spreading agent mixture can provide improved shine enhancement of the hair.

Also, the spreading agent will preferably reduce the surface tension by at least about 2 dynes/cm<sup>2</sup>, preferably at least about 3 dynes/cm<sup>2</sup>, even more preferably at least about 4 dynes/cm<sup>2</sup>, most preferably at  
15 least about 5 dynes/cm<sup>2</sup>.

The surface tension of the mixture of the polysiloxane fluid and the spreading agent, at the proportions present in the final product, is preferably 30 dynes/cm<sup>2</sup> or less, more preferably about 28 dynes/cm<sup>2</sup> or less most preferably about 25 dynes/cm<sup>2</sup> or less. Typically the surface tension will be in the range of from about 15 to about 30, more typically from about 18 to about 28, and most generally from  
20 about 20 to about 25 dynes/cm<sup>2</sup>.

The weight ratio of the highly arylated polysiloxane fluid to the spreading agent will, in general, be between about 1000:1 and about 1:1, preferably between about 100:1 and about 2:1, more preferably between about 50:1 and about 2:1, most preferably from about 25:1 to about 2:1. When fluorinated surfactants are used, particularly high polysiloxane: spreading agent ratios may be effective due to the  
25 efficiency of these surfactants. Thus is contemplated that ratios significantly above 1000:1 may be used.

References disclosing examples of some suitable silicone fluids for use in the shampoo compositions include U.S. Patent 2,826,551, U.S. Patent 3,964,500, U.S. Patent 4,364,837, British Patent 849,433, and Silicon Compounds, Petrarch Systems, Inc. (1984), all of which are incorporated herein by reference.

30 Silicone resins can be included in the silicone conditioning agent. These resins are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or difunctional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated  
35 into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and

5 tetrafunctional siloxane monomer units (and hence, a sufficient level of crosslinking) such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinyl-chlorosilanes, and tetrachlorosilane, with the methyl-substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art.

Background material on silicones including sections discussing silicone fluids, gums, and resins, as well as manufacture of silicones, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, incorporated herein by reference.

15 Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as "MDTQ" nomenclature. Under this system, the silicone is described according to presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit  $(\text{CH}_3)_3\text{SiO}_{0.5}$ ; D denotes the difunctional unit  $(\text{CH}_3)_2\text{SiO}$ ; T denotes the trifunctional unit  $(\text{CH}_3)\text{SiO}_{1.5}$ ; and Q denotes the quadri- or tetra-functional unit  $\text{SiO}_2$ . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyls, amines, hydroxyls, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone (or an average thereof) or as specifically indicated ratios in combination with molecular weight complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

25 The silicone resins for use herein which are preferred are MQ, MT, MTQ, MDT and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

35 The weight ratio of the nonvolatile silicone fluid, having refractive index below 1.46, to the silicone resin component, when used, is preferably from about 4:1 to about 400:1, preferably this ratio is from about 9:1 to about 200:1, more preferably from about 19:1 to about 100:1, particularly when the silicone fluid component is a polydimethylsiloxane fluid or a mixture of polydimethylsiloxane fluid and

polydimethylsiloxane gum as described above. Insofar as the silicone resin forms a part of the same phase in the compositions hereof as the silicone fluid, i.e. the conditioning active, the sum of the fluid and resin should be included in determining the level of silicone conditioning agent in the composition.

#### Optional Suspending Agent

5 The shampoo compositions of the present invention may further comprise a suspending agent at concentrations effective for suspending the optional silicone hair conditioning agent, or other water-insoluble material, in dispersed form in the shampoo compositions. Such concentrations range from about 0.1% to about 10%, preferably from about 0.3% to about 5.0%, by weight of the shampoo compositions.

Optional suspending agents include crystalline suspending agents that can be categorized as acyl  
10 derivatives, long chain amine oxides, or combinations thereof, concentrations of which range from about 0.1% to about 5.0%, preferably from about 0.5% to about 3.0%, by weight of the shampoo compositions. When used in the shampoo compositions, these suspending agents are present in crystalline form. These suspending agents are described in U.S. Patent 4,741,855, which description is incorporated herein by reference. These preferred suspending agents include ethylene glycol esters of fatty acids preferably  
15 having from about 16 to about 22 carbon atoms. More preferred are the ethylene glycol stearates, both mono and distearate, but particularly the distearate containing less than about 7% of the mono stearate. Other suitable suspending agents include alkanol amides of fatty acids, preferably having from about 16 to about 22 carbon atoms, more preferably about 16 to 18 carbon atoms, preferred examples of which include stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic  
20 monoethanolamide stearate. Other long chain acyl derivatives include long chain esters of long chain fatty acids (e.g., stearyl stearate, cetyl palmitate, etc.); glyceryl esters (e.g., glyceryl distearate) and long chain esters of long chain alkanol amides (e.g., stearamide diethanolamide distearate, stearamide monoethanolamide stearate). Long chain acyl derivatives, ethylene glycol esters of long chain carboxylic acids, long chain amine oxides, and alkanol amides of long chain carboxylic acids in addition to the  
25 preferred materials listed above may be used as suspending agents. For example, it is contemplated that suspending agents with long chain hydrocarbyls having C<sub>8</sub>-C<sub>22</sub> chains may be used.

Other long chain acyl derivatives suitable for use as suspending agents include N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof (e.g., Na, K), particularly N,N-di(hydrogenated) C<sub>16</sub>, C<sub>18</sub> and tallow amido benzoic acid species of this family, which are commercially available from Stepan  
30 Company (Northfield, Illinois, USA).

Examples of suitable long chain amine oxides for use as suspending agents include alkyl (C<sub>16</sub>-C<sub>22</sub>) dimethyl amine oxides, e.g., stearyl dimethyl amine oxide

Other suitable suspending agents include xanthan gum at concentrations ranging from about 0.3% to about 3%, preferably from about 0.4% to about 1.2%, by weight of the shampoo compositions. The use  
35 of xanthan gum as a suspending agent in silicone containing shampoo compositions is described, for

example, in U.S. Patent 4,788,006, which description is incorporated herein by reference. Combinations of long chain acyl derivatives and xanthan gum may also be used as a suspending agent in the shampoo compositions. Such combinations are described in U.S. Patent 4,704,272, which description is incorporated herein by reference.

5 Other suitable suspending agents include carboxyvinyl polymers. Preferred among these polymers are the copolymers of acrylic acid crosslinked with polyallylsucrose as described in U.S. Patent 2,798,053, which description is incorporated herein by reference. Examples of these polymers include Carbopol 934, 940, 941, and 956, available from B. F. Goodrich Company .

10 Other suitable suspending agents include primary amines having a fatty alkyl moiety having at least about 16 carbon atoms, examples of which include palmitamine or stearamine, and secondary amines having two fatty alkyl moieties each having at least about 12 carbon atoms, examples of which include dipalmitoylamine or di(hydrogenated tallow)amine. Still other suitable suspending agents include di(hydrogenated tallow)phthalic acid amide, and crosslinked maleic anhydride-methyl vinyl ether copolymer.

15 Other suitable suspending agents may be used in the shampoo compositions, including those that can impart a gel-like viscosity to the composition, such as water soluble or colloiddally water soluble polymers like cellulose ethers (e.g., methylcellulose, hydroxybutyl methylcellulose, hydroxypropylcellulose, hydroxypropyl methylcellulose, hydroxyethyl ethylcellulose and hydroxyethylcellulose), guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, and other  
20 thickeners, viscosity modifiers, gelling agents, etc. Mixtures of these materials can also be used.

#### Method of Use

The shampoo compositions of the present invention are used in a conventional manner for cleansing and conditioning hair or skin. An effective amount of the composition for cleansing and conditioning the hair or skin is applied to the hair or skin, that has preferably been wetted with water, and  
25 then rinsed off. Such effective amounts generally range from about 1gm to about 50gm, preferably from about 1gm to about 20gm. Application to the hair typically includes working the composition through the hair such that most or all of the hair is contacted with the composition.

This method for cleansing and conditioning the hair or skin comprises the steps of:

30 a) wetting the hair or skin with water, b) applying an effective amount of the shampoo composition to the hair or skin, and c) rinsing the applied areas of skin or hair with water. These steps can be repeated as many times as desired to achieve the desired cleansing and conditioning benefit.

#### Examples

The shampoo compositions illustrated in Examples I-XV are specific embodiments of the shampoo compositions of the present invention, but are not intended to be limiting thereof. Other  
35 modifications can be undertaken by the skilled artisan without departing from the spirit and scope of this

invention. These exemplified embodiments of the shampoo compositions of the present invention provide cleansing of hair and improved hair conditioning performance.

All exemplified compositions can be prepared by conventional formulation and mixing techniques. Component amounts are listed as weight percents and exclude minor materials such as diluents, filler, and so forth. The listed formulations, therefore, comprise the listed components and any minor materials associated with such components.

**Component**

**Example Number**

	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>
Ammonium Laureth-3 Sulfate	10.00	10.00	10.00	10.00	10.00
Ammonium Lauryl Sulfate	6.00	6.00	6.00	6.00	6.00
Polyquaternium-37 (2)	0.50	0.25	0.75	0.50	0.50
Cocamide MEA	0.80	0.80	0.80	0.80	0.80
Cetyl Alcohol	0.42	0.42	0.42	0.42	0.42
Stearyl Alcohol	0.18	0.18	0.18	0.18	0.18
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
Dimethicone (1)	1.00	1.00	1.00	1.50	2.00
Perfume Solution	0.60	0.60	0.60	0.60	0.60
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Color Solution (ppm)	64	64	64	64	64
Water and Minors					
	----- q.s. to 100% -----				

ComponentExample Number

	<u>VI</u>	<u>VII</u>	<u>VIII</u>	<u>IX</u>	<u>X</u>
Ammonium Laureth-3 Sulfate	10.00	10.00	12.00	10.00	12.00
Ammonium Lauryl Sulfate	6.00	6.00	4.00	6.00	4.00
Polyquaternium-37 (2)	0.50	0.25	0.50	0.50	0.25
Cocamide MEA	0.80	0	0.68	0.80	0.68
Cetyl Alcohol	0.42	0.42	0.42	0	0.42
Stearyl Alcohol	0.18	0.18	0.18	0	0.18
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
Dimethicone (1)	0	0	1.00	1.00	1.00
Perfume Solution	0.60	0.60	0.60	0.60	0.60
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Color Solution (ppm)	64	64	64	64	64
Water and Minors					

----- q.s. to 100% -----

ComponentExample Number

	<u>XI</u>	<u>XII</u>	<u>XIII</u>	<u>XIV</u>	<u>XV</u>
Ammonium Laureth-3 Sulfate	5.80	5.80	5.80	5.80	5.80
Ammonium Lauryl Sulfate	5.70	5.70	5.70	5.70	5.70
Cocamidopropylbetaine	2.50	2.50	2.50	2.50	2.50
Polyquaternium-37 (2)	0.50	0.25	0.50	0.75	1.00
Cocamide MEA	0.68	0.68	0.68	0.68	0.68
Cetyl Alcohol	0.42	0.42	0.42	0.42	0
Stearyl Alcohol	0.18	0.18	0.18	0.18	0
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
Dimethicone (1)	1.50	1.50	0	1.00	0
Perfume Solution	0.60	0.60	0.60	0.60	0.60
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Color Solution (ppm)	64	64	64	64	64
Water and Minors					

----- q.s. to 100% -----

(1) Dimethicone is a 40(gum)/60(fluid) weight ratio blend of SE-76 dimethicone gum available from General Electric Silicones Division and a dimethicone fluid having a viscosity of 350 centistokes.

5

(2) Polyquaternium-37 is a crosslinked cationic polymer available from Allied Colloids.

What is claimed is:

1. A stable conditioning shampoo composition comprising:

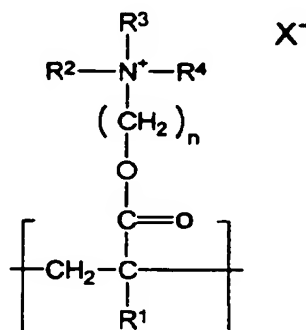
(A) from 5% to 50%, preferably 8% to 30%, by weight of an anionic surfactant component selected from the group consisting of anionic surfactants, zwitterionic or amphoteric surfactants having an attached group that is anionic at the pH of the composition, and combinations thereof;

(B) from 0.025% to 5% by weight of an organic, crosslinked, cationic polymer having a cationic charge density of from 4 meq/gm to 7 meq/gm, preferably from 4.2 meq/gm to 5.5 meq/gm, and wherein the cationic polymer consists essentially of a crosslinking agent and a monomer unit selected from the group consisting of dialkylaminoalkyl acrylamides, dialkylaminoalkyl methacrylamides, dialkylaminoalkyl acrylates, dialkylaminoalkyl methacrylates, and combinations thereof, wherein each of the monomer units is cationic at the pH of the composition; and

(C) from 20% to 94% by weight of water.

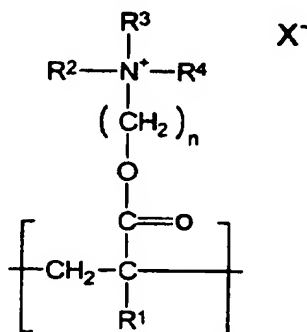
2. The shampoo composition of Claim 1 wherein the anionic surfactant component is an alkyl sulfate, alkyl ether sulfate surfactant, or combination thereof.

3. The shampoo composition of Claim 1 wherein the monomer units are selected from the group consisting of cationic substituted dialkylaminoalkyl acrylates, dialkylaminoalkyl methacrylates, and combinations thereof, preferably the monomer units conform to the formula



wherein  $\text{R}^1$  is hydrogen, methyl or ethyl; each of  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are independently hydrogen or a short chain alkyl having from 1 to 8 carbon atoms, preferably from 1 to 5 carbon atoms;  $n$  is positive integer having a value of from 1 to 8, preferably from 1 to 4; and  $\text{X}$  is an anionic counterion.

4. The shampoo composition of Claim 3 wherein  $R^2$ ,  $R^3$  and  $R^4$  are independently a short chain alkyl having from 1 to 2 carbon atoms.
5. A stable conditioning shampoo composition comprising:
- (A) from 5% to 50%, preferably 8% to 30%, by weight of an anionic surfactant component selected from the group consisting of anionic surfactants, zwitterionic or amphoteric surfactants having an attached group that is anionic at the pH of the composition, and combinations thereof;
  - (B) from 0.025% to 5% by weight of an organic, crosslinked, cationic polymer having a cationic charge density of from 4 meq/gm to 7 meq/gm, 4.2 meq/gm to 5.5 meq/gm, and wherein the cationic polymer consists essentially of a crosslinking agent and a monomer unit selected from the group consisting of dialkylaminoalkyl acrylamides, dialkylaminoalkyl methacrylamides, dialkylaminoalkyl acrylates, dialkylaminoalkyl methacrylates, and combinations thereof, wherein each of the monomer units is cationic at the pH of the composition;
  - (C) from 0.01% to 10% by weight of a silicone hair conditioning agent; and
  - (D) from 20% to 94% by weight of water.
6. The shampoo composition of Claim 5 wherein the silicone hair conditioning agent comprises an insoluble, non volatile, polyalkylsiloxane fluid, preferably polydimethylsiloxane.
7. The shampoo composition of Claim 5 wherein the anionic surfactant component is alkyl sulfate, alkyl ether sulfate, or combinations thereof.
8. The shampoo composition of Claim 5 wherein the monomer units are selected from the group consisting of cationic substituted dialkylaminoalkyl acrylates, dialkylaminoalkyl methacrylates, and combinations thereof, preferably the monomer units conform to the formula





wherein  $R^1$  is hydrogen, methyl or ethyl; each of  $R^2$ ,  $R^3$  and  $R^4$  are independently hydrogen or a short chain alkyl having from 1 to 8 carbon atoms, preferably from 1 to 5 carbon atoms; n is positive integer having a value of from 1 to 8, preferably from 1 to 4; and X is an anionic counterion.

9. The shampoo composition of Claim 8 where ; each of  $R^2$ ,  $R^3$  and  $R^4$  are independently a short chain alkyl having from 1 to 5 carbon atoms; n is positive integer having a value of from 1 to 4.

10. The shampoo composition of Claim 9 wherein  $R^1$  is hydrogen or methyl and  $R^2$ ,  $R^3$  and  $R^4$  are independently a short chain alkyl having from 1 to 2 carbon atoms.

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/03695

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 A61K7/06 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 627 217 A (HELENE CURTIS) 7 December 1994 see claims 1,2,7,8,10 see page 5, line 3-8 ---	1-10
X	WO 95 09600 A (PROCTER & GAMBLE) 13 April 1995 see claims 1,3,7 see page 9, line 24 - page 10, line 15 see page 17, line 23 - page 18, line 18 see page 21, line 17-26 ---	1,3-6, 8-10
X	WO 94 21224 A (L'OREAL) 29 September 1994 see claims 1,2,4,8,9,11 see page 7, line 16-25 ---	1,3-6, 8-10
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

7 August 1997

Date of mailing of the international search report

21.08.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Peeters, J

# INTERNATIONAL SEARCH REPORT

Initial Application No

PCT/US 97/03695

**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 124 245 A (KAO) 15 February 1984 see page 2, line 8-20 see page 3, line 57 - page 4, line 10 -----	1-4

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/03695

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 627217 A	07-12-94	US 5417965 A	23-05-95
		AU 6310694 A	24-11-94
		CA 2123634 A	18-11-94
		JP 7069845 A	14-03-95
		NO 941842 A	18-11-94
		NZ 260543 A	27-06-95
		US 5556616 A	17-09-96
-----			
WO 9509600 A	13-04-95	NONE	
-----			
WO 9421224 A	29-09-94	FR 2702653 A	23-09-94
		AT 146072 T	15-12-96
		AU 676723 B	20-03-97
		AU 6260694 A	11-10-94
		CA 2158341 A	29-09-94
		CN 1119413 A	27-03-96
		DE 69401125 D	23-01-97
		DE 69401125 T	03-04-97
		EP 0689419 A	03-01-96
		ES 2095753 T	16-02-97
		HU 73867 A	28-10-96
		JP 8508024 T	27-08-96
		PL 310442 A	11-12-95
		US 5637306 A	10-06-97
-----			
GB 2124245 A	15-02-84	JP 1343493 C	29-10-86
		JP 59020396 A	02-02-84
		JP 61010517 B	29-03-86
		CA 1212297 A	07-10-86
		EP 0101920 A	07-03-84
		HK 54587 A	31-07-87
		US 4534892 A	13-08-85
-----			

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**